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PHOSPHORUS FILLINGS FOR MUNITIONS

Progress Report on Work Performed in the Period July 1 to

September 30, 1947, under Contract W-18-035-CWS-1318

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By Chester C. Becker
Signature and Grade
Date 23 October 61

Wilson Dam, Alabama

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Tennessee Valley Authority
Chemical Engineering Department
Chemical Research and Engineering Branch
Chemical Research Division

# PHOSPHORUS FILLINGS FOR MUNITIONS

Progress Report on Work Performed in the Period July 1 to September 30, 1947, under Contract W-16-036-CWS-1318

By

J. C. Brosheer, F. A. Lenfesty, and P. L. Imes

Wilson Dam, Alabama

Tennessee Valley Authority
Chemical Engineering Department
Wilson Dam, Alabama
December 3, 1947

Commanding Officer
Chemical Corps Technical Command
Building 330
Army Chemical Center, Maryland

Attention: Chief, Munitions Division

Gentlemen:

Transmitted herewith are six copies of the fifth quarterly progress report on our studies of phosphorus fillings for munitions. The report covers work performed under contract W-18-035-CWS-1318 during the period July 1 to September 30, 1947.

Very truly yours,

TENNESSEE VALLEY AUTHORITY

K. L. Elmore

K. L. Elmore, Chief
Chemical Research Division

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# PHOSPHORUS FILLINGS FOR MUNITIONS

## Progress Report on Work Performed in the Period July 1 to September 30, 1947, under Contract W-18-035-CWS-1318

## SUMMARY

Investigations of the properties of various fillings in which granules of phosphorus are cemented with a fluid binder that subsequently sets in the munition to form a solid filling have indicated that plaster of paris, Duralon, and Thiokol LP-2 are the most promising of the various experimental binders. These binders will be used exclusively in immediate further study of fillings based upon granulated ~~phosphorus~~ P.

~~Flame retardants proved of little effect on the performance of experimental fillings.~~

The present method of measuring the thermal instability of the fillings by determination of the unbalance of a filled munition after storage on its side under desert conditions appears to be satisfactory. ~~A pendulum-type balance will be constructed and the longitudinal shift of the center of gravity of the fillings, as well as the lateral shift, will be determined.~~ The thermal stability of the fillings will be tested in glass containers, as well as in M15 grenades, with ~~the objective of~~ providing a visual check on the movement of ~~the~~ components of the various fillings upon exposure to ~~abnormally~~ high storage temperatures.

Fillings composed of mixtures of red and white ~~phosphorus~~ P, particularly mixtures that result from substantially complete conversion of white ~~phosphorus~~ P to massive red ~~phosphorus~~ P within the munition, appear to be very promising. Methods of conversion of white to red phosphorus will be studied, both at controlled (atmospheric and superatmospheric) pressures and in sealed munitions in which a maximum pressure of 630 pounds per square inch and a maximum temperature of 590° C. are to be expected.

Because of the difficulty experienced in an objective evaluation of the smokes produced by experimental fillings in M15 grenades, it is most desirable that 4.2-inch CM shells be filled with the more promising fillings and submitted to the Army Chemical Center for storage and performance tests. Such a test program certainly should include several shells filled with massive red phosphorus, prepared in place by rapid conversion of a charge of white phosphorus in the sealed munition.

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In the 3-month period covered by this progress report, work was confined largely to those fillings comprising granulated white phosphorus and various binders that had appeared both to be thermally stable and to perform satisfactorily in grenade firing tests. A study of methods for the preparation of fillings containing red phosphorus was begun.

Because of the uncertainty involved in the prediction of performance of a given filling in a larger munition from the performance of the filling in M15 grenades, a few 4.2-inch CM shells were filled with TVA experimental fillings and subjected to performance tests at Army Chemical Center. Although these tests were carried out somewhat later than the period nominally covered by this report, the results are pertinent to the present work, and they are included in this report.

## GRANULATION OF WHITE PHOSPHORUS

As the scale of operation was enlarged and the need for granulated phosphorus increased, the jet granulator mentioned in previous progress reports was modified to increase its capacity. The present form of the apparatus is shown in Figure 1.

In operation of the granulator, the receiver is [illegible]rly filled with ice water, and the granulating tube is connected thereto. Into the granulating tube is poured 200 cc. of a saturated solution of white phosphorus in 95 per cent alcohol, then enough ice water to raise the liquid level to the point at which the side-arm overflow is attached. The ice bath is placed around the receiver. The jacket is put in place and filled with hot water, and hot water is poured into the granulating tube to the level of the overflow. The phosphorus reservoir is then inserted into the granulating tube at an elevation that places the tip of the jet just below the surface of the water. Molten phosphorus, under water, is poured from a dipper through a funnel into the phosphorus reservoir. The phosphorus flows from the jet as a rapid stream, which promptly breaks into separate spherules that fall through the column of water and solidify in the lower part of the granulating tube. When the receiver is filled with granulated phosphorus, addition of phosphorus is discontinued, the hot water jacket is drained and [illegible], and the granulating tube is emptied through the lower drain. The [illegible]r is then emptied, and the process is repeated.

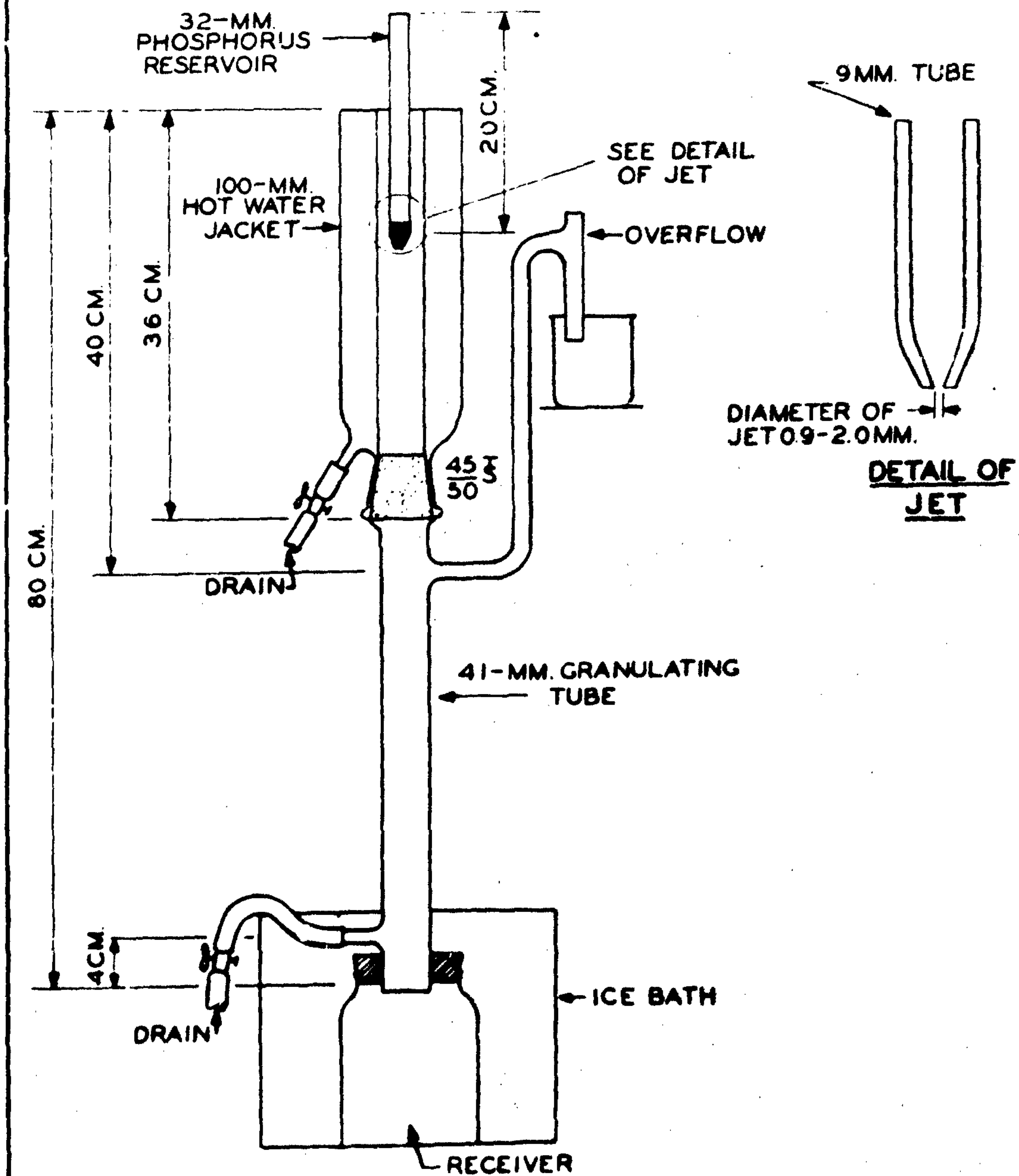


**FIGURE I**
**PHOSPHORUS GRANULATOR**

The molten phosphorus is added at a temperature of 70° to 75° C. The water added to the jacket is between 80° and 85° C. When the temperature of the water in the top of the granulating tube falls to about 50° C., the phosphorus flowing through the jet forms strings instead of spherules, and the phosphorus may solidify in the jet.

The jet is held in a rubber stopper in the bottom of the phosphorus reservoir. Three jets may be used simultaneously in an apparatus of the size shown in Figure 1. Each jet, under a head of molten phosphorus and water that varies from 5 to 15 cm., passes roughly 100 grams of phosphorus per minute. Since the granulated phosphorus occupies an apparent volume of approximately 1 cc. per gram, a 2700-cc. receiver can be filled in about 10 minutes when three jets are used.

The jets are made from 9-mm. glass tubing that is constricted to capillary size and cut off squarely at the constriction. Jets with orifices larger than 2.0 mm. in diameter pass phosphorus too rapidly for the formation of separate drops, and jets with orifices smaller than 0.8 mm. in diameter plug easily and pass phosphorus too slowly to be of practical use.

The size of the spherules is proportional roughly to the size of the orifice of the jet. Because of the intermittent feed of molten phosphorus to the phosphorus reservoir, and because of variation in the temperature of the molten phosphorus and of the water in the top of the granulating tube, the particle size of the granules formed by a given size of jet is quite variable in the present apparatus. Approximate screen analyses of granules formed by three sizes of jets are listed in Table I. The minus 8-mesh fraction (last column in table) contains about 17 per cent, by weight, of material that will pass a 16-mesh screen.

The granulation could be made continuous by addition to the receiver of a tube through which the granulated phosphorus could be removed. The tube would have to extend above the level of the overflow, and provision would have to be made for maintaining the water in the tube at the level of the overflow. The granulated phosphorus could be lifted to a container filled with water to the same level as that of the overflow.

Firing tests of fillings based upon granulated white phosphorus indicated that performance was related roughly to the phosphorus content of the filling. To get the maximum amount of granulated phosphorus into [illegible] space, granules of various sizes must be mixed. A mixture of 30 [illegible] weight of granulated phosphorus of the type prepared in the pilot [illegible] the Army Chemical Center with 70 parts of plus 4-mesh granulated

phosphorus of the type prepared by the jet method formed a minimum-void mixture with 35 per cent void space. The void space in various mixtures of the three size fractions of granules that were separated from the products of jet granulation are shown in Figure 2. The over-all experimental error in the preparation of a given mixture and measurement of the interstitial space in the mixture generally did not exceed 2 per cent.

TABLE I

Screen Analyses of Granulated Phosphorus

Prepared with Jets of Various Diameters

| Orifice dia., mm. | Screen analysis, weight per cent | | |
|---|---|---|---|
| | +4 mesh | -4 +8 mesh | -8 mesh |
| 2.0 | 40 | 50 | 10 |
| | 29 | 57 | 14 |
| 1.4 | 2 | 65 | 33 |
| | 8 | 76 | 16 |
| 0.9 | 5 | 58 | 37 |
| | 3 | 52 | 45 |

The granulated phosphorus produced in the present pilot plant at the Army Chemical Center is somewhat difficult to handle because of its pronounced tendency to float on water. On the other hand, the plus 4-mesh fraction of jet-granulated phosphorus imparts an undesirable lumpiness to fillings in which it is incorporated. A mixture of jet-granulated phosphorus comprising 60 per cent by weight of minus 4- plus 8-mesh granules and 40 per cent of minus 8-mesh granules has been adopted tentatively as a standard mixture for use in experimental fillings. Since this mixture contains about 37 per cent voids, as shown in Figure 2, it supplies 97 per cent as much phosphorus in a given volume as would be supplied by a mixture containing 35 per cent voids, the apparent practical minimum of void space in granulated phosphorus.

Although mixtures of granulated phosphorus that contain 37 [illegible] obviously supply only 63 per cent of the amount of phosphorus [illegible] supplied by the same volume of massive white phosphorus, the [illegible] the granulated phosphorus affects the burning to the extent that the granulated phosphorus often produces a more effective screening smoke than does an equal volume of massive white phosphorus.

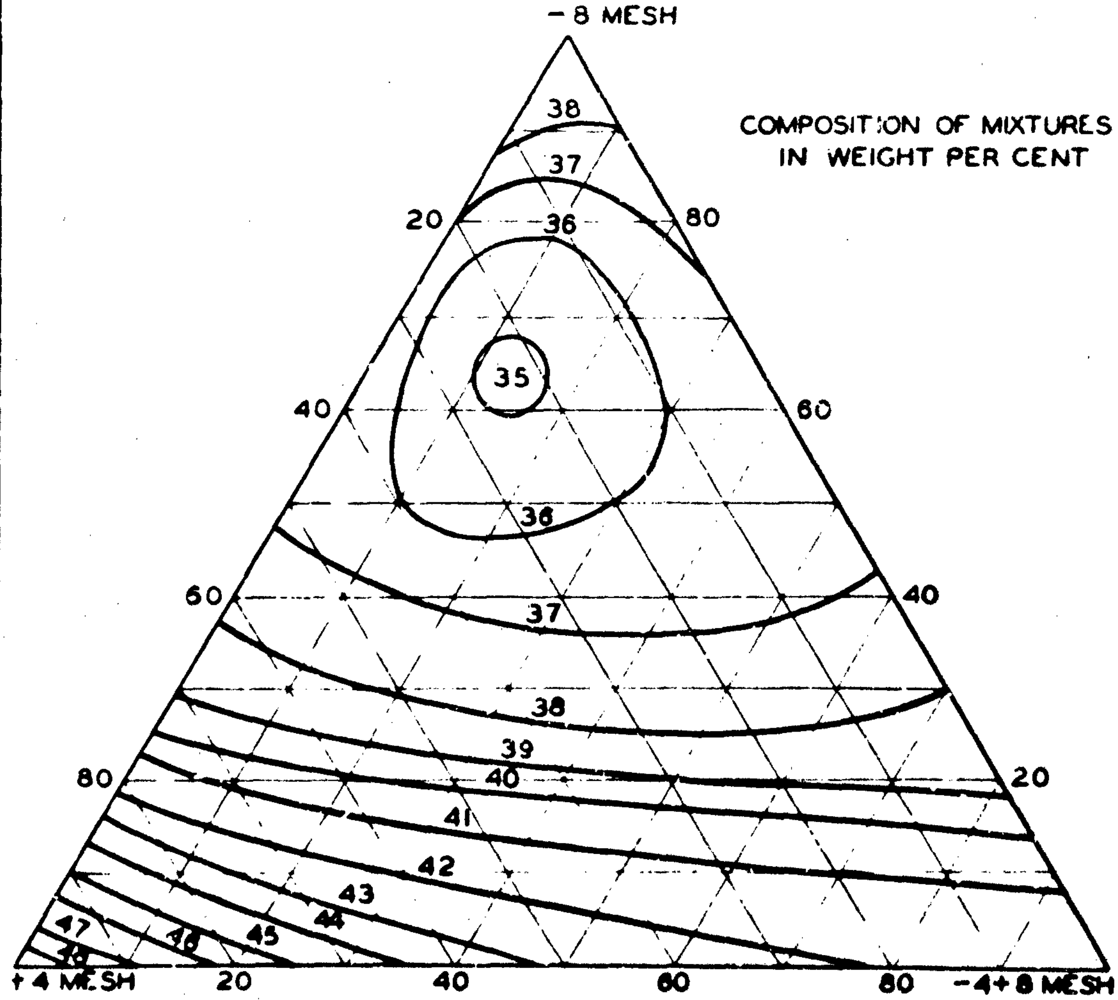


FIGURE 2
PER CENT VOIDS IN MIXTURES OF THREE PARTICLE SIZES
OF JET - GRANULATED WHITE PHOSPHORUS

## BINDERS FOR GRANULATED WHITE PHOSPHORUS

The procedure for preparation of fillings from granulated phosphorus and charging the fillings into M15 grenades has been standardized as follows:

The granulated phosphorus is weighed and transferred, under water, to a 51-mm. glass tube with a perforated stainless steel disc in its lower end. The phosphorus is dewatered by blowing carbon dioxide through the tube from the top. If removal of substantially all the water is desired because of the binder to be used, the dewatered phosphorus is washed two or three times with alcohol or acetone, and carbon dioxide is blown through the tube between washings.

The binder, in a fluid state, is weighed into a 600-cc. beaker. The dewatered phosphorus is dumped into the beaker, and the mixture is stirred with a spatula and transferred to the grenade in an atmosphere of carbon dioxide. A short-stemmed powder funnel facilitates the introduction of the filling into the grenade. The filling is rodded through the funnel with a stirring rod.

### Furetone

Furetones are furane-type resins produced by the Irvington Varnish and Insulator Company of Irvington, New Jersey. Their resins 5510 and 5510A5 are thermosetting and may be set at room temperature with their accelerator 5243. Preliminary tests, in which the resins were cured at room temperature in air, showed the Furetone 5510 with 10 per cent accelerator set to a rubbery solid in 24 hours and to a hard solid in 48 hours. Furetone 5510A5 with 5 per cent accelerator set to a rubbery solid in 3 days at 40° C., and to a spongy, rubbery solid in about 7 days at room temperature. Furetone 5510A5 initially appeared to be suitable for use as a binder for phosphorus fillings; when used for this purpose, however, it set only to a semifluid rubbery material with a cohesion markedly greater than its adhesion. Furetone 5510 was too viscous for use as a binder for granulated white phosphorus.

### Thiokol LP-2

At the suggestion of the Thiokol Corporation, the setting of their [illegible]lymer Thiokol LP-2 with furfural and formic acid was modified by [illegible]ion of "chain-stoppers," such as mercaptoethanol. In the presence of chain-stoppers, the polymer sets to a somewhat tacky, rubbery mass that

is noticeably less rigid than the solid to which the polymer sets in the absence of chain-stoppers. Thiokol LP-2, with incorporations of mercaptoethanol, has been used as a binder for phosphorus fillings, but the fillings have not been subjected to firing tests.

## Binders Containing Flame Retardants

Fillings in which the binder was Duralon or Thiokol LP-2 were modified by the incorporation of 15 per cent of ammonium oxalate into the binder, the objective being to retard the rate of combustion. The ammonium oxalate had little effect on the performance of the fillings.

## FILLINGS CONTAINING RED PHOSPHORUS

In August 1944, TVA filled forty 4.2-inch CM shells with a mixture of approximately 50 per cent red and 50 per cent white phosphorus and returned them to Edgewood Arsenal for firing tests. A Report of Test, dated at Edgewood Arsenal on October 6, 1944, indicates that the shells performed satisfactorily and compared favorably with PWP-filled shells.

Work at Edgewood Arsenal on the preparation of red phosphorus fillings for munitions is reported in TDMR No. 793, January 6, 1944. Some work was done on the conversion of white to red phosphorus in glass tubes at temperatures below the boiling point of white phosphorus (280° C.), but the results were somewhat erratic and did not appear promising. The Arsenal also converted white phosphorus to red phosphorus in sealed shells. Although the operation is somewhat hazardous, no difficulties in the preparation were reported. The shells are said to have performed very well in firing tests.

The experience of the Arsenal with fillings containing red phosphorus and the experience of TVA in the conversion of white phosphorus to red phosphorus appeared to warrant further exploration of red phosphorus as a component of phosphorus fillings for munitions.

## Formation of Red Phosphorus at Atmospheric Pressure

TVA research on the conversion of liquid white phosphorus to red phosphorus has shown that as the proportion of red phosphorus increases the mixture remains fluid at the melting point of white phosphorus until the red phosphorus constitutes between 45 and 60 per cent of the mixture.

At some critical composition, which varies for reasons unknown, the mixture solidifies at 280° C. and cannot be melted at temperatures below the melting point of red phosphorus, 590° C. at 43 atmospheres.

A 6-hour heat of liquid white phosphorus at 280° C. converts an average of about 40 per cent of the phosphorus to the red form. In a continuous operation designed to produce fluid mixtures of red and white phosphorus for charging into munitions, this time of reaction is not necessarily excessive. Any mixture of red and white phosphorus fluid enough to be charged into a munition probably would be unstable physically in desert storage. Such fluid mixtures might be used to advantage, however, in a method involving further conversion to red phosphorus in the munition.

Iodine and sulfur catalyze the conversion of liquid white phosphorus to solid red phosphorus. Laboratory experiments, in glass, showed that white phosphorus containing 2 per cent sulfur, on boiling for 4.5, 5.5, and 6.5 hours, was converted to mixtures containing 57, 59, and 59 per cent, respectively, of red phosphorus. All three preparations remained solid, without separation of white phosphorus, in boiling water. Several M15 grenades were charged with white phosphorus containing 2 per cent sulfur and heated under reflux condensers at 280° C. for 1, 2, 3, 4, and 6 hours. The grenades that had been heated for 6 hours contained a thermally stable filling; all the other fillings behaved as fluids at 65° C.

## Formation of Red Phosphorus in Sealed Grenades

Grenades were charged with about 370 grams of white phosphorus containing 2 per cent sulfur. The burster-well threads were doped with Aquadag, an aqueous suspension of colloidal graphite, and the well was screwed into place. The closure was quite effective; only a few grenades leaked in subsequent operations. A 36-inch length of 1/4-inch pipe was attached to the top of the burster well as a means of support for the grenade. A thermocouple was passed through the pipe to the bottom of the burster well. The grenades were heated singly in a vertical tube furnace behind a barricade. Provision was made for raising or lowering the grenade through the furnace tube by remote control.

The grenades were heated at the rate of 3° to 5° C. per minute. [illegible] temperature registered by the thermocouple in the burster well [illegible] about 280° C., the exothermic conversion reaction took control and [illegible] temperature to about 560° C. in from 2 to 5 minutes. In subsequent runs, a bucket of water was placed under the furnace, and when the temperature in the grenade began to rise abruptly, the grenade was lowered

into the water. The quenching reduced the maximum temperature to about 540° C. In one run, the grenade jammed in its downward passage from the furnace tube and was lifted above the furnace. The temperature rose to 562° C., and the grenade exploded. The body of the grenade separated from the top at the silver-soldered joint.

The grenades in which the red phosphorus conversion was effected under pressure were bulged at the bottom. From measurements of the deflection of the bottoms of three grenades that had not been quenched during the conversion, it was calculated, from formulae developed for cylindrical vessels with flat ends, that the maximum pressure in the grenades was of the order of 300 to 500 pounds per square inch. The vapor pressure of white phosphorus, as shown in Figure 3, is between 500 and 600 pounds per square inch at the maximum temperature of about 560° C. recorded during the conversion.

The available thermal data on red and white phosphorus are inadequate for close approximation of the maximum temperature that would be reached in the conversion of a large amount of white phosphorus to red phosphorus in a closed container. The heat of the exothermic conversion is about 16,000 calories per mole of $P_4$. When the grenades were quenched during the conversion, the maximum temperature was about 540° C. When the grenades were not quenched but remained in the furnace, which presumably had an effective temperature of about 300° C., the maximum temperature was about 560° C. Hence, it may be assumed that if no heat were lost from the grenade during the conversion, the maximum temperature probably would not exceed 560° C. This temperature, and the corresponding vapor pressure of white phosphorus, 600 pounds per square inch, are the probable limits to which a closed container would be subjected in the conversion of white to red phosphorus.

Since red phosphorus melts at 590° C. under a pressure of 43 atmospheres (630 pounds per square inch), the heat of fusion of the red phosphorus, estimated to be about 16,000 calories per mole of $P_4$, would absorb all the heat of transformation of white to red phosphorus, thus setting 590° C. as the apparent maximum temperature that possibly could be obtained in the conversion of white to red phosphorus in a closed vessel initially heated to any temperature below 590° C.

To test the effect of various amounts of sulfur in the catalysis [illegible] phosphorus conversion, grenades were filled with 770 grams of white [illegible]us containing 0, 1, and 2 per cent sulfur. In grenades containing [illegible]ur, the rapid conversion began at 320° to 330° C., and the maximum temperature reached in the quenched grenades was 563° C. With 1 per cent sulfur in the phosphorus, the rapid conversion began at 280° to 290° C. when the grenade was placed in a cold furnace and heated, and at temperatures between 260° and 280° C. when the grenade was placed in a warm

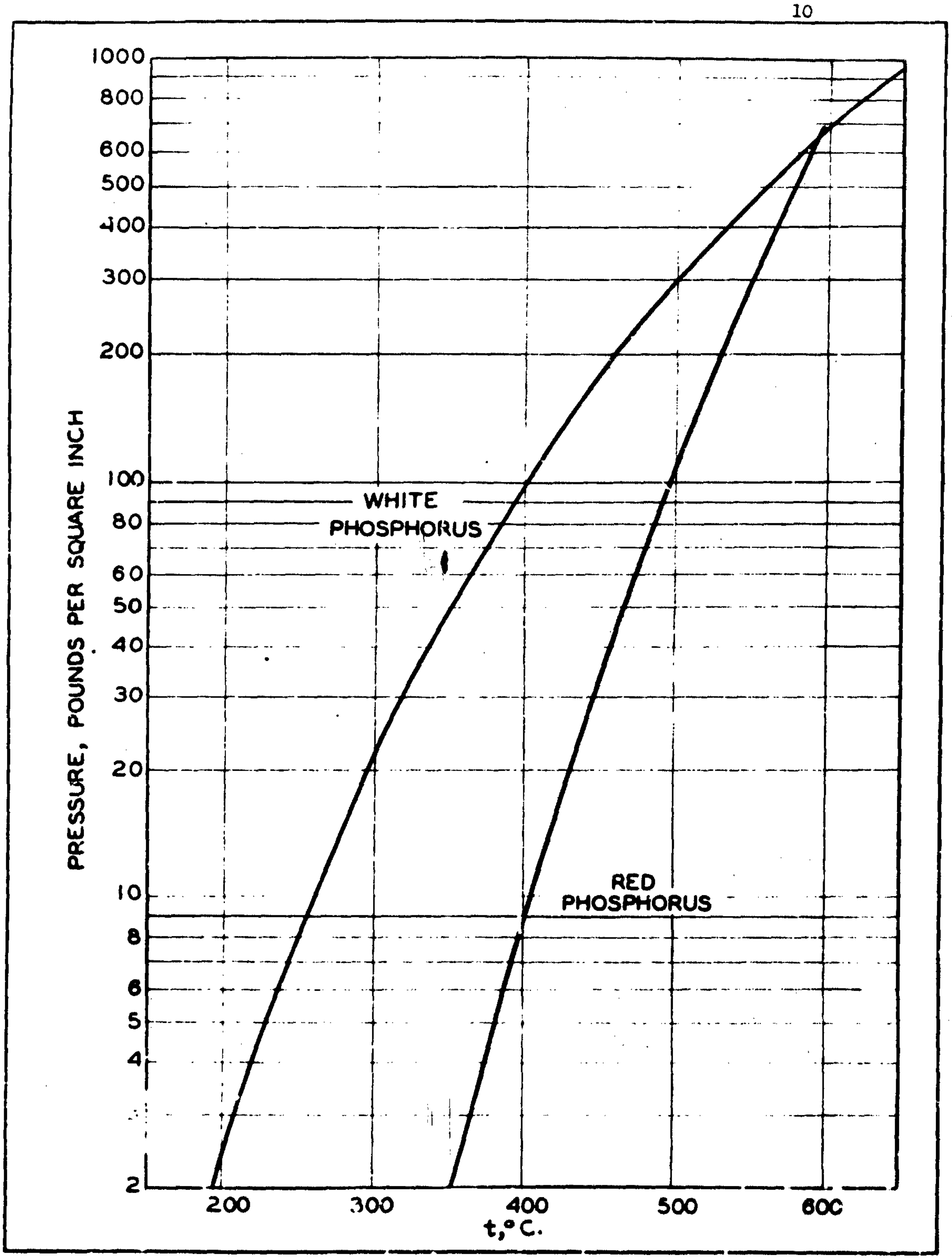


FIGURE 3
VAPOR PRESSURE OF PHOSPHORUS

(about 150° to 200° C.) furnace and heated; the maximum temperature in the quenched grenades varied from 494° to 544° C. With 2 per cent sulfur, the rapid conversion started at temperatures between 270° and 290° C., and the maximum temperature in the quenched grenades varied between 530° and 550° C. Operation generally was smoothest with 1 per cent sulfur, and this amount of catalyst is recommended for the conversion. The sulfur is added conveniently in the form of the liquid phosphorus-sulfur eutectic containing 80 per cent phosphorus and 20 per cent sulfur.

One grenade in which red phosphorus was prepared from white phosphorus containing no sulfur and one in which the charge contained 1 per cent sulfur were cut open. Both products were brick-red, massive solids that nearly filled the grenades. The product of the catalyzed conversion contained some very small occluded drops of what appeared to be the liquid phosphorus-sulfur eutectic. Portions of each of the products were crushed, with considerable difficulty, in a porcelain mortar under water and will be analyzed to determine the proportions of red and white phosphorus.

In three of the conversion experiments, quenching of the grenade halted the rapid conversion that apparently had been started. Subsequent heating of each of the three grenades resulted in normal rapid conversion with the attainment of normal maximum temperatures. In the absence of cooling coils within the phosphorus mass, control of the extent of conversion by quenching therefore appears to be practically impossible. The red phosphorus prepared by this method ignites readily and burns freely when the munition is burst by an exploder, however, and there is no apparent reason for attempting to control the amount of conversion.

Because of the uncertainty that the conversion actually has started when a temperature of say, 290° C., is reached, the in-place method of forming red phosphorus in fillings for munitions would involve certain difficulties in large-scale production. If the munition could with certainty withstand an internal pressure of 600 pounds per square inch at 600° C., it could be filled with white phosphorus and carried on a conveyor belt through an oven maintained at some temperature, say 320° C., at which the rapid conversion is certain to be initiated.

It is reported in TDMR No. 793 that the rapid conversion was initiated in 4.2-inch CM shells that were allowed to remain in ovens heated to temperatures between 224° and 265° C. until conversion was complete, but the length of time required at any of these temperatures is not stated. The preparation of a fluid mixture of roughly 40 per cent red and 60 per cent white phosphorus might be feasible in equipment similar to that in the TVA pilot plant for conversion of liquid white phosphorus to red phosphorus. Shells filled with such a mixture might be sealed and heated to complete the conversion. The use of such mixtures probably would reduce materially the temperature and attendant pressure generated in the rapid conversion.

## THERMAL STABILITY TESTS

Filled M15 grenades were tested for thermal stability by maintaining them at 55° C. for 8 hours, while lying on their sides, and subsequently cooling them in the same position. The unbalance caused by the shift in the position of the filling was measured on grenades containing certain plaster-of-paris, Duralon, and red phosphorus fillings to yield the results listed in Table II.

The plaster-of-paris fillings appear to be consistently stable, regardless of the amount of water used in the preparation of the plaster. Grenades containing red phosphorus, formed in place by conversion of white phosphorus, apparently are unaffected by exposure to any temperatures at which munitions might be stored. The marked thermal instability of the Duralon fillings in the present series may perhaps be attributed to insufficient aging of the fillings before the tests were made, or to the use of an insufficient amount of binder, although it was thought that enough binder was always used to ensure a small amount of liquid resin standing on top of the mass of phosphorus granules when the filling was placed in the grenade.

TABLE II

Thermal Stability Tests of Phosphorus Fillings in M15 Grenades

(Grenades heated 3 hours at 65° C.)

| No. | Filling | Age, days | Wt., g. Fill-ing | Wt., g. Gre-nade | Wt. to balance, g. | Shift of center of gravity, mm. Grenade | Shift of center of gravity, mm. Filling |
|---|---|---|---|---|---|---|---|
| **Plaster of paris with 185 grams of stirrer-granulated phosphorus** | | | | | | | |
| C3A | Plaster 100; water 60 | 6 | 337 | 684 | 5 | 0.22 | 0.45 |
| C3C | | 6 | 359 | 721 | 7 | 0.29 | 0.59 |
| C4A | Plaster 100; water 80 | 5 | 349 | 691 | 7 | 0.30 | 0.60 |
| C4C | | 5 | 351 | 694 | 3 | 0.13 | 0.26 |
| C5D | Plaster 100; water 100 | 5 | 310 | 650 | 10 | 0.46 | 0.97 |
| **Red phosphorus converted in sealed grenades** | | | | | | | |
| R1B | Not quenched | 1 | 292 | 630 | 2 | 0.10 | 0.21 |
| R2B | Quenched | 1 | 374 | 717 | 0 | nil | nil |
| **Red phosphorus converted at atmospheric pressure** | | | | | | | |
| R3D | Heated 1 hour | 1 | 381 | 751 | 57 | 2.3 | 4.5 |
| R3B | Heated 2 hours | 4 | 374 | 774 | 59 | 2.3 | 4.7 |
| R3C | Heated 3 hours | 4 | 383 | 772 | 26 | 1.1 | 2.2 |
| R3E | Heated 4 hours | 1 | 375 | 745 | 31 | 1.3 | 2.5 |
| R3A | Heated 6 hours | 5 | 374 | 761 | nil | nil | nil |
| **Duralon** | | | | | | | |
| E3C | Stirrer-gran and +4 mesh WP | 4 | 318 | 664 | 35 | 1.6 | 3.3 |
| E3A | | 14 | 317 | 664 | 37 | 1.7 | 3.5 |
| E4B | Stirrer-gran. WP | 4 | 258 | 602 | 34 | 1.7 | 4.0 |
| E4C | Stirrer-gran. WP | 14 | 275 | 598 | 30 | 1.5 | 3.3 |
| [illegible] | [illegible]-mesh WP | 5 | 285 | 634 | 25 | 1.2 | 2.6 |
| [illegible] | 4-mesh WP | 14 | 299 | 644 | 38 | 1.8 | 3.8 |
| E6A | -4 +8-mesh WP | 4 | 281 | 623 | 47 | 2.3 | 5.0 |
| E6B | -4 +8-mesh WP | 14 | 287 | 635 | 52 | 2.5 | 5.4 |

## FIRING TESTS

Despite attempts to devise a standard, objective method of test of phosphorus fillings, evaluation of the performance of such fillings remains substantially a subjective procedure, the value of which depends largely upon the experience of the observer. Since the tests are outdoors, the apparent performance is affected markedly by the prevailing atmospheric conditions.

The purpose of the present experimental work is to develop phosphorus fillings that will perform satisfactorily in munitions such as the 4.2-inch CM shell, which has a capacity of about 8 pounds of massive white phosphorus. This munition is supposed to produce, in winds moving at 10 or more miles per hour, an opaque screen about 20 feet high and 100 yards long that persists for at least 60 seconds. To conserve time and material, however, the M15 grenade has been selected as the test munition.

The grenade has a capacity of 0.9 pound of massive white phosphorus. Satisfactory performance of a phosphorus filling in the grenade has been defined tentatively at the Army Chemical Center as the yield of an opaque screen about 15 feet high and 10 yards long that persists for 20 seconds. In firing tests of the munitions, the observer is stationed about 200 yards from the burst of the 4.2-inch shell or 50 to 80 yards from the burst of the grenade; the line between the observer and the burst preferably is normal to the direction of the wind.

Prediction of the performance of a given phosphorus filling in a shell on the basis of the performance of the same filling in a grenade is complicated by several factors. A much larger proportion of the filling is consumed in the burst of the grenade than is consumed in the burst of the shell, hence the screen generated by the scattered fragments from the shell is relatively more dense and lasts longer than the screen from the grenade. Furthermore, fragments from a grenade may produce streamers of smoke that do not form an obscuring screen, but it often appears that a proportionately larger number of similar fragments from a shell might produce a very satisfactory screen. Shells perform best in winds moving at velocities of 10 or more miles per hour, where the tendency of the smoke generated by the burning phosphorus to rise and dissipate into the air is overbalanced by the wind which holds it down on the ground. At lower wind velocities, the screen may be broken by the smoke rising off the ground.

Grenades, on the other hand, perform best in winds moving at velocities between 2 and 4 miles per hour; at lower velocities the variable effect of the prevailing atmospheric conditions on the rate of rise and dissipation of the smoke makes difficult a determination of the ability of the scattered fragments of the filling to maintain a screening smoke. At wind velocities greater than 4 miles per hour, the smoke produced in the burst of grenades tends to move downwind in a body, and the smoke generated by the burning fragments is insufficient to produce a continuous screen between the initial cloud and the site of the burst.

An examination of photographs of smokes produced by experimental fillings in grenades shows that the fragments scattered in the burst of this munition burn fast enough to sustain an obscuring screen in winds moving not faster than 3 miles per hour. In fact, a wind velocity of 3 miles per hour is looked upon as a maximum. The average sustaining velocity of the smokes rated as good in the present report was 1.4 miles per hour.

To take advantage of somewhat uniform weather conditions, the firing tests were made between 5:30 and 7:30 A. M. No correlation was apparent between the ground-air temperature gradient and performance of the fillings. Good screens were obtained when the air was 2° F. warmer than the ground as well as when the ground was 8° F. warmer than the air. The tests were discontinued when the average wind velocity increased to about 4 miles per hour. As the wind picked up, however, it came in gusts, and a few grenades were fired in winds as fast as 7 miles per hour.

The performance of the experimental fillings in the present report was assumed to be good when the burst produced an obscuring screen at least 10 yards wide that persisted for at least 20 seconds. Fillings that gave screening smokes that persisted for 11 to 19 seconds were rated as fair, and those that gave screening smokes that persisted less than 11 seconds were rated as poor.

It was impractical to set up a target downwind from the bursts, because in relatively still air the screen might never cover the target, and in fast winds the obscuring screen would drift past the target much faster than the screen was dissipated. Thus, in still air the screen obscured a target directly behind the burst, in winds faster than 4 miles per hour the screen was assumed to obscure a moving target, and only in winds between 2 and 4 miles per hour could an evaluation be made on a basis comparable to that used in the evaluation of screens from 4.2-inch CM shells. Only about 50

t of those grenades rated as good were fired in winds having velocities

ptimum range.

## Effect of Particle Size of Granulated White Phosphorus

The amount of smoke that can be produced by a phosphorus filling obviously is directly proportional to the amount of combustible phosphorus initially present in the filling. The amount of useful smoke is a function also of the size and rate of burning of the fragments of the filling that are scattered in the burst, and these characteristics, in turn, are affected by the particle size of the granulated phosphorus of which the filling is composed.

Figure 2 shows that various mixtures of different sizes of granules of phosphorus may be used to obtain a given percentage of voids, so that the same weight of phosphorus may be charged into a given space with either of several possible mixtures. Several fillings composed of mixtures of various proportions of different sizes of phosphorus granules were prepared with plaster of paris and with Duralon to test the effect of particle size of the granulated phosphorus on the performance of the fillings. The results, which are listed in Table III, indicate that the finer particle sizes give better performance than the coarser sizes; the good performance of the relatively small weight of the very fine stirrer-granulated phosphorus when used alone is particularly noteworthy.

### TABLE III

### Effect of Particle Size of Granulated White Phosphorus on Performance of Experimental Fillings

| Screen analysis of gran. WP, wt. % of indicated mesh size | | | | Phosphorus charged, g. | No. of grenades tested | Per cent of grenades producing screens of indicated persistence | | |
|---|---|---|---|---|---|---|---|---|
| +4[a] | -4+8[a] | -8[a] | -30+80[b] | | | >15 sec. | 10-15 sec. | 0-10 sec. |
| Plaster-of-paris fillings | | | | | | | | |
| 0 | 60 | 40 | 0 | 258 | 2[c] | 100 | 0 | 0 |
| 0 | 0 | 0 | 100 | 185 | 4 | 50 | 25 | 25 |
| 0 | 15 | 85 | 0 | 256 | 4 | 50 | 25 | 25 |
| 70 | 0 | 0 | 30 | 266 | 4 | 25 | 25 | 50 |
| 60 | 0 | 40 | 0 | 206 | 4 | 25 | 0 | 75 |
| 100 | 0 | 0 | 0 | 204 | 4 | 25 | 0 | 75 |
| Duralon fillings | | | | | | | | |
| | [illegible] | 0 | 30 | 266 | [illegible] | 100 | 0 | 0 |
| | 0 | 0 | 100 | 185 | 4 | 50 | 25 | 25 |
| 0 | 60 | 40 | 0 | 259 | 2[c] | 50 | 0 | 50 |
| 0 | 100 | 0 | 0 | 223 | 4 | 0 | 75 | 25 |
| 100 | 0 | 0 | 0 | 204 | 4 | 0 | 75 | 25 |

[a] Jet-granulated.
[b] Stirrer-granulated at Army Chemical Center.
[c] Tested at Army Chemical Center.

Effect of Binder

Fillings were prepared by incorporation of selected mixtures of various particle sizes of granulated phosphorus into different binders. Table IV shows the results of firing tests of these fillings. The Duralon fillings appeared to give the best performance in tests at Wilson Dam, and the plaster-of-paris fillings were rather disappointing in view of their very promising performance in previous tests. (In quite limited and inconclusive firing tests of some of these experimental fillings at the Army Chemical Center on October 16, 1947, a date shortly after the period covered in detail by the present report, plaster of paris, phenolic casting resins, and Thiokol LP-2 appeared to form fillings with granulated phosphorus that performed well in grenades, whereas the performance of Duralon fillings was relatively poor.)

Grenades filled with massive white phosphorus were used as controls in the firing tests. Of these grenades, 60 per cent were good and 40 per cent were fair.

Plasticized White Phosphorus (PWP): One of the most disturbing phenomena encountered in the evaluation of experimental phosphorus fillings in grenades is the consistently poor performance of PWP in firing tests at Wilson Dam. The material performs well in shells, and is reported to perform satisfactorily in grenades in tests at the Army Chemical Center.

A sample of PWP, received from the Army Chemical Center and allowed to stand for two months under water in the original container, had a specific gravity of 1.362. Assuming that the specific gravity of the xylene-rubber gel was 0.88, and that the PWP was free of occluded water or gas, the PWP then contained 68 per cent phosphorus by weight. Four grenades were filled with 281 grams each of the PWP, four were filled with a mixture of 227 grams of the PWP and 89 grams of plus 4-mesh granulated phosphorus, and four were filled with a mixture of 185 grams of the PWP and 131 grams of plus 4-mesh granulated phosphorus. The total weight of phosphorus per grenade in the three series was then 191, 242, and 257 grams, respectively.

In firing tests of the grenades containing the PWP, all four grenades containing PWP alone were rated as poor; three of the four grenades containing the smaller amount of coarse granulated phosphorus were rated as fair, and one was rated as poor; and all four grenades containing the larger amount of coarse granulated phosphorus were rated as fair. Although addition [illegible]se granulated phosphorus to PWP probably is not a practical method of [illegible]ing a phosphorus filling, the results of the firing tests indicate, at [illegible], that the performance of such fillings is improved as the phosphorus content of the filling is increased.

## TABLE IV

### Effect of Binder on Performance of Experimental Fillings

### Based upon Granulated White Phosphorus

| Binder | No. of grenades tested | Per cent of grenades producing screens of indicated persistence >19 sec. | 11-19 sec. | 0-10 sec. |
|---|---|---|---|---|
| 185 g. WP; 100% -30 +80 mesh stirrer-granulated. | | | | |
| Duralon | 4 | 50 | 25 | 25 |
| Plaster 100, water 100 | 4 | 50 | 25 | 25 |
| Plaster 100, water 60 | 4 | 25 | 50 | 25 |
| Plaster 100, water 30 | 4 | 0 | 100 | 0 |
| 266 g. WP; 70% +4 mesh jet-granulated, 30% -30 +80 mesh stirrer-granulated. | | | | |
| Duralon | [illegible] | 100 | 0 | 0 |
| Thiokol LP-2 | 4 | 50 | 50 | 0 |
| Urea-furfural[a] | 4 | 50 | 25 | 25 |
| Furetone | 10 | 40 | 50 | 10 |
| Plaster 100, water 100 | 4 | 25 | 25 | 50 |
| Urea-formaldehyde[a] | 4 | 25 | 25 | 50 |
| Bakelite phenolic resin | 5 | 20 | 20 | 60 |
| Durez phenolic resin | 4 | 0 | 50 | 50 |
| 258 g. WP; 60% -4 +8 mesh and 40% -8 mesh jet-granulated[b]. | | | | |
| Plaster 100, water 100 | [illegible] | 100 | 0 | 0 |
| Phenolic casting resin | 2 | 100 | 0 | 0 |
| Thiokol LP-2 | 1 | 100 | 0 | 0 |
| Duralon | 2 | 50 | 0 | 50 |

[a] Laboratory preparation.
[b] Tested at Army Chemical Center.

Plaster-of-Paris fillings: Although fillings in which granules of phosphorus are cemented with plaster of paris have performed somewhat [illegible]ally in firing tests at [illegible]son Dam, these fillings are the only [illegible]ntal TWA fillings prepared with granulated phosphorus that appear to [illegible]mally stable. In firing tests at the Army Chemical Center, two grenades and two 4.2-inch CM shells containing this type of filling all performed satisfactorily. [illegible] on these fillings is being continued.

The plaster-of-paris fillings have been modified by the use of a [illegible] per cent emulsion of white phosphorus in an 8 per cent aqueous solution of polyvinyl alcohol as the source of water for setting the plaster. Such fillings have performed with consistent excellence in grenade tests both at Wilson Dam and at the Army Chemical Center, and two mortar shells carrying this filling also performed quite well. Although the polyvinyl alcohol apparently inhibits somewhat the setting of the plaster of paris, the single sample of this filling that has been tested for thermal stability appeared to be as stable as any of the unmodified plaster-of-paris fillings.

Duralon Fillings: Fillings containing Duralon casting resin as the binder for granulated white phosphorus performed well in firing tests at Wilson Dam but failed of consistently good performance in either grenades or shells in tests at the Army Chemical Center. The thermal instability exhibited by these fillings has since been shown to be attributable, at least in part, to an insufficient amount of binder. Additional fillings containing larger proportions of Duralon will be prepared and tested for thermal stability and for performance in firing tests.

Thiokol-LP-2 Fillings: Thiokol LP-2, cured with 20 per cent of furfural and 4 per cent of formic acid, is the only rubbery binder for granulated phosphorus that has been tested extensively at TVA. Fillings containing this binder were more stable thermally than the latest batches of Duralon fillings, but they were markedly less stable than plaster-of-paris fillings. Thiokol fillings have performed fairly well in firing tests at Wilson Dam and at the Army Chemical Center.

Furetone Fillings: Although Furetone 5510[illegible] was set in 7 days at room temperature to a rubbery solid, either the lack of oxygen or the presence of phosphorus in the fillings in which this resin was the binder apparently inhibited the set of the resin so that only a weak, tacky binder was produced. The fillings were markedly unstable thermally, and significant amounts of the binder worked out of the grenades through the threads of the burster wells. Fillings bound with Furetone performed fairly well in firing tests but were rated as unsatisfactory because of their marked thermal instability.

Phenolic Resin Fillings: Fillings in which various phenolic casting resins were used as binders for granulated phosphorus have performed with consistent poorness in firing tests at Wilson Dam, but two grenades that were charged with these fillings and tested at the Army Chemical Center performed quite well. Marblette casting resin formed thermally stable fillings, other phenolic resins formed unstable fillings.

Laboratory Resin Fillings: Laboratory resins prepared from urea and furfural and from urea and formaldehyde have been used as binders for granulated phosphorus in a few grenades. The fillings performed fairly well in firing tests, but the rapid disintegration of the binders at the temperature of the thermal stability test makes these fillings unsatisfactory.

[illegible]. It was reported [illegible] that incorporation of a salt, such as ammonium oxalate, which decomposes endothermically at relatively low temperatures, in a phenolic resin filling markedly improved the performance of the filling in firing tests. The salt acted as an inhibitor in the curing of the phenolic resin, however, with the result that the cured binder was soft and weak. Investigation of the effect of ammonium oxalate on various binders showed that both Buralon and Thiokol LP-2 were unaffected by additions of ammonium oxalate. Fillings bound with Buralon and Thiokol, both with and without additions of ammonium oxalate, were test fired but the added salt gave no improvement in performance. It is concluded that the improvement in the performance of the phenolic resin to which ammonium oxalate had been added was due to the modification of the physical properties of the binder, rather than to the decomposition of the flame retarding salt when the grenade was exploded.

<u>Red Phosphorus Fillings</u>: Three mortar shells that had been filled by [illegible] in [illegible] with a mixture of 50 per cent white phosphorus and 50 per cent red phosphorus performed well in firing tests at the Army Chemical Center on October [illegible], 1947.

Two grenades in which a portion of the white phosphorus filling had been converted to red phosphorus by boiling at atmospheric pressure for 6 hours were rated as only fair in firing tests at Wilson Dam. These two fillings were thermally stable, however, and probably contained at least 50 per cent red phosphorus. It is believed that these fillings would have performed well in shells, for both grenades produced fragments of filling that sustained active combustion for 1 to 5 minutes. Although smoke from these fragments did not produce an obscuring screen, it appeared that, had the same proportion of a shell filling been scattered as fragments of the same size, the smoke produced by the much larger number of fragments from the larger charge would have made a very satisfactory screen.

Grenade fillings comprised almost entirely of massive red phosphorus that had been formed in place in sealed grenades by conversion of white phosphorus performed poorly in firing tests at Wilson Dam. On the other hand, two grenades containing similar fillings performed excellently in firing tests at the Army Chemical Center. The poor performance at Wilson Dam was characterized by the scattering of relatively large fragments of massive red phosphorus that burned well but produced too little smoke to maintain an obscuring screen. Had there been a larger number of these fragments, as presumably would have been produced in the explosion of a [illegible] CM shell containing the same filling, the screen probably would [illegible] satisfactory.

## REVIEW OF RESULTS AND PLANS FOR FURTHER WORK

Of the various experimental phosphorus fillings prepared and tested by CWS, the most promising appear to be those in which granulated phosphorus is bound with ordinary plaster of paris, or with plaster of paris to which an emulsion of phosphorus in an aqueous solution of polyvinyl alcohol is added as the hydrating agent, and those in which massive red phosphorus is prepared in place in the sealed munition through conversion of an initial charge of white phosphorus. Fillings containing Durolon and Thiokol LP-2 as binder will be studied further, although the poor thermal stability of these two types of fillings threatens their eventual elimination from consideration.

Additional work on those fillings in which granulated phosphorus is cemented by fluid binders that solidify to form rigidly solid fillings will include determinations of the optimum amount of binder and the optimum mixture of the various particle sizes of granulated phosphorus, as related both to the thermal stability of the munition and to the performance of the munition in firing tests.

The lateral shift of the center of gravity of the filling from the longitudinal axis of the filled munition incident to storage of the munition on its side under desert conditions appears to give a good indication of the thermal stability of the filling. A pendulum-type balance will be constructed to permit a determination of the longitudinal shift of the center of gravity as well. Data obtained with this device will be of value in determining whether the shift in center of gravity of an unstable filling is due to flow of phosphorus from the solid sponge formed by the setting of the binder around the phosphorus granules or to movement of the binder itself. The tests will be made on experimental fillings in both M15 grenades and glass containers. Sinc the charges in glass containers will be visible, they will aid in interpretation of the measurements made on grenades.

The performance of the various red phosphorus fillings has been good enough to warrant further investigation of methods for conversion of white to red phosphorus in munitions. Among the phases of the problem that will receive the most attention are the rates of conversion at various temperatures above the boiling point of white phosphorus (280° C.); these conversions will have to be carried out under pressures greater than atmospheric pressure, but not in an entirely closed system. It is hoped that massive red phosphorus fillings can be prepared in sealed 4.2-inch CM shells containing an initial charge of white phosphorus.

Since correlation of the performance of fillings, particularly red phosphorus fillings, in M15 grenades with performance in 4.2-inch CM shells is not readily apparent, it appears that final test of experimental fillings should be made in shells. To that end, groups of shells containing the promising TVA experimental fillings will be prepared and submitted to the Army Chemical Center for storage and performance tests. Work in the immediate future will be devoted largely to study of methods of preparation and determination of thermal stabilities of the various promising experimental fillings with the objective of charging the shells with fillings that reasonably may be expected to give the best performance possible for each type of filling.